ELSEVIER

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 16 (2012) 895 – 900

Energy Procedia

2012 International Conference on Future Energy, Environment, and Materials

Distribution and Enrichment Evaluation of Cadmium in the Sediments of Canon River Mouth, Taiwan

Chiu-Wen Chen, Chih-Feng Chen, Cheng-Di Dong *

Department of Marine Environmental Engineering, National Kaohsiung Marine University, Kaohsiung 81157, Taiwan, R. O. C.

Abstract

The distribution, enrichment, and potential risk of cadmium (Cd) in the sediments of Canon River mouth, Taiwan were investigated. Sediment samples from 12 stations in the Canon River mouth were collected and characterized for Cd, aluminum, organic matter, and grain size. The results show that samples collected at all monitoring stations near the mouth of Canon River contain 0.20–3.85 mg/kg of Cd with average of 1.74±1.08 mg/kg. The spatial distribution of Cd reveals that the Cd concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor region. This indicates that upstream industrial and municipal wastewater discharges along the river bank are major sources of pollution. The accumulation factor and potential ecological risk index indicate that the sediments at Canon River mouth have the most serious degree of Cd accumulation and the serious ecological potential risk.

Keywords: cadmium; sediment; river mouth; enrichment factor

1. Introduction

The metals generated by anthropogenic activities cause more environmental pollution than naturally occurring metals [1]. After entering a water body, heavy metals will be carried over to sea so that the river mouth and regions along seashore become the ultimate resting place for these metals being transported in the environment. Hence, the river mouth region, harbor and seashore with dense population and industries usually become heavily polluted by toxic metals [2]. Cadmium (Cd) is extremely toxic and highly bio-accumulative [3]-[4]; its presence threatens the water ecological environment. Therefore, much research effort has been directed toward the distribution of Cd in water environment. Anthropogenic activities

* Corresponding author. Tel.: +886-7-3617141-3762; fax: +886-7-365-0548.
E-mail address: cddong@mail.nkmu.edu.tw.

 doi:10.1016/j.egypro.2012.01.143

including municipal wastewater discharges, agriculture, mining, incineration, and discharges of industrial wastewater are the major source of Cd pollution [5]. Cadmium has low solubility in aqueous solution; it is easily adsorbed on water-borne suspended particles. After a series of natural processes, the water-borne Cd finally accumulates in the sediment, and the quantity of Cd contained in the sediment reflect the degree of pollution for the water body [6].

Canon River flows through a southern Taiwan industrial city (Kaohsiung City). In previous years, the river received untreated municipal and industrial wastewater discharges causing serious deterioration of the river water quality and the environmental quality near the river mouth to threaten the water environmental ecological system seriously. The objective of this study is to investigate the Cd distribution in the surface sediment near Canon River mouth so that the degree of Cd accumulation and potential ecological risk can be evaluated.

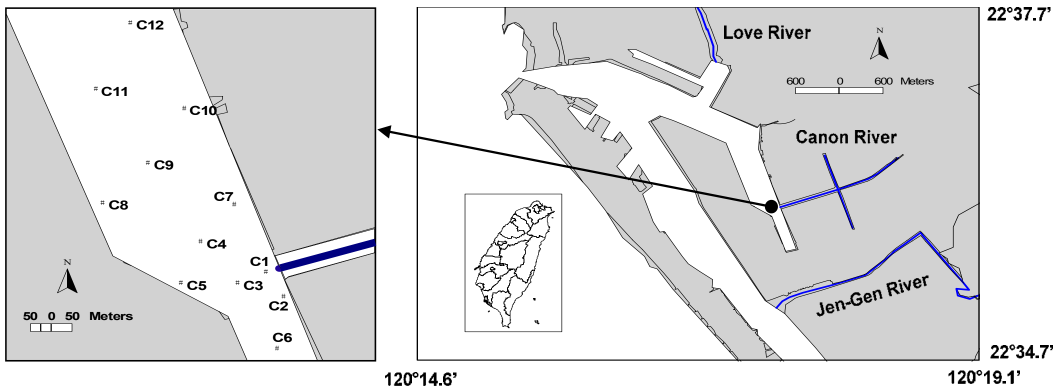

Fig. 1. Map of the study area and sampling locations.

2. Materials and methods

Sediment samples were collected at 12 stations near Canon River mouth (Fig. 1) in May, 2009 with Ekman Dredge Grab aboard a fishing boat. The collected samples were temporarily placed in polyethylene bottles that had been washed with acid; the bottles were stored in a dark ice chest filled with crushed ice. After transported back to the laboratory, a small portion of the sample was subject to direct water content analysis (105°C), and the remaining portion was preserved in -20°C freezer to be analyzed later. Prior to being analyzed, each sample was lightly crushed with a wooden board, and then screened through 1 mm nylon net to remove particles with diameters larger than 1 mm. One portion of the screened portion was subject to particle size analyses using a Coulter LS Particle Size Analyzer. Another portion was washed with ultra-pure water to remove sea salt; the salt-free particles were dried naturally in a dark place, grounded into fine powder with mortar and pestle made of agate, and then analyzed for organic matter, total grease (TG), Cd, and aluminum (Al). Details of the sediment characteristics (e.g. particle size, water content, OM, TG, and Al) are listed elsewhere [7].

Statistical data analyses include average, standard deviation, maximum and minimum. The linear correlation of Pearson technique was used to analyze the correlation between sediment characteristics and Cr concentration implemented with the SPSS 12.0 software. In this study, the enrichment factor (EF) and geo-accumulation index (I_{geo}) were applied to evaluate the degree of Cd pollution and the associated potential ecological risk index (PERI). EF is defined as: EF = $(X/Al)_{sediment}/(X/Al)_{crust}$, where (X/Al) is the ratio of Cd to aluminum. The average aluminum content in the earth crust was excerpted from the data published by Taylor (1964) [8]. The I_{geo} is defined as: $I_{geo} = \log_2 (C_n/1.5B_n)$ [9], where C_n is the measured content of Cd, and B_n is the background content of Cd in the average shale. The potential ecological risk index PERI is defined as: PERI = PI × T_i [10], where PI is the pollution index of Cd (C_i/C_f); T_i is its corresponding coefficient, i.e. 30 for Cd [11]; C_i is the measure concentration of Cd in sediment; C_f is the background concentration of Cd. In this study, the average Cd concentration in the bottom core sediment (80 cm) of 0.08 mg/kg [12] was taken as the Cd background concentration.

3. Results and discussion

3.1. Distribution of cadmium in sediments

Fig 1 shows the distribution of Cd contents and enrichment factor in the surface sediments of Canon River mouth. All sediment samples collected at Canon River mouth contain 0.20–3.85 mg/kg of Cd with an average of 1.74±1.08 mg/kg. Concentration distributions of Cd in Canon River mouth sediment shown in Fig 2 reveal that the sediment Cd content is relatively higher near the river mouth, and gradually decreases in the direction toward the harbor. Because Canon River is subject to upstream discharges of un-treated domestic and industrial wastewaters, the pollutants are transported by river flow and finally accumulate near the river mouth. Some pollutants may drift with sea current to be dispersed into open sea [11].

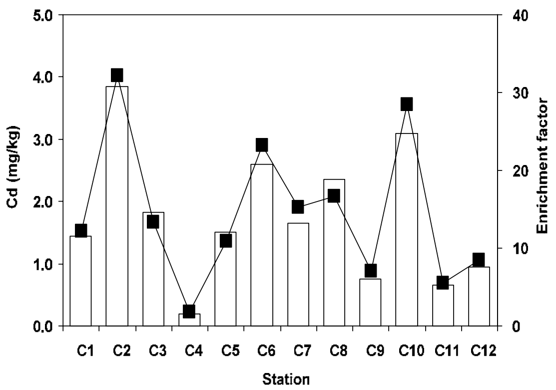

Fig. 2. Cadmium concentrations (bar chart) and enrichment factor (scatter plot with connect line) distribution in surface sediments at 11 monitoring stations.

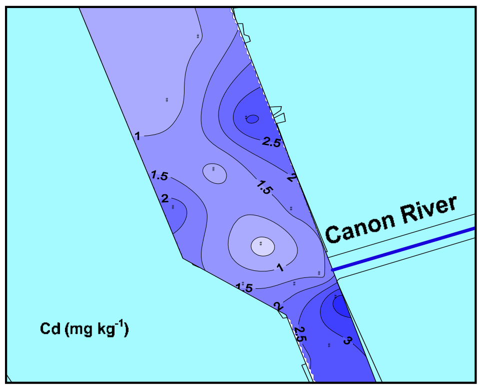

Fig. 3. Distribution of Cd contents in surface sediment of Canon River mouth region.

Coefficient of the Pearson correlation between the sediment characteristics and Cd content is shown in Table 1. The sediment Cd content is obviously correlated to TG ($p<0.05$) but not to OM ($p>0.05$) or particle size ($p<0.05$) indicating that OM and particle siz are not major factor to control the Cd distribution [13]. The environmental condition of the river mouth in this study region such as discharges of upstream pollutants, and alternation between fresh water and sea water may be very complicated so that very little correlation between the sediment Cd concentration and other sediment characteristics is observed to exist.

Table 1 Pearson correlation coefficients among sediment characteristics and Cd concentrations (n = 12)

	Clay	Silt	Sand	Water content	OM	TG	Al
Silt	0.732[a]						
Sand	-0.789[a]	-0.996[a]					
Water content	0.357	0.636[b]	-0.619[b]				
OM	-0.021	0.433	-0.388	0.844[a]			
TG	-0.100	0.470	-0.412	0.682[b]	0.853[a]		
Al	0.055	0.366	-0.337	0.076	0.169	0.531	
Cd	0.263	0.555	-0.534	0.481	0.435	0.640[b]	0.191

[a]Correlation is significant at the 0.01 level (2-tailed); [b]Correlation is significant at the 0.05 level (2-tailed).

3.2. Enrichment factor

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination [14-16]. This evaluating technique is carried out by normalizing the metal concentration based on geological characteristics of sediment. Aluminum is a major metallic element found in the earth crust; its concentration is somewhat high in sediments and is not affected by man-made factors. Thus, Al has been widely used for normalizing the metal concentration in sediments [17-18]. When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa. The EF value can be classified into 7 categories [19]: no enrichment for EF <1, minor for EF <3, moderate for EF = 3–5, moderately severe for EF = 5–10, severe for EF = 10–25, very severe for EF = 25–50, and extremely severe for EF >50. Table 2 and Fig. 2(a) show EF values of the surface sediment Cd for the Canon River mouth region; the Cd concentration is consistent with the Cd EF value for all sampling stations, and all EF values are greater than 1. This indicates that the sediment Cd has enrichment phenomenon with respect to the earth crust and that all Cd originates from man-made sources. Except Station C4 that has minor enrichment of Cd, all other sampling stations are classified as either moderately severe or severe or very severe enrichment. Based on the I_{geo} data and Muller's geo-accumulation indexes, the contamination level with respect to Cd at each station is ranked in Table 2. Based on the above observations, sediments at the Canon River mouth was moderate polluted. These results point out that the sediment near Canon River experiences severe accumulation of Cd that originates from the upstream sources of pollution.

Table 2. EF and Igeo classes of Cd for each station studied at the Canon River mouth

Station	EF	EF class[a]	I_{geo}	I_{geo} class[b]	Station	EF	EF class[a]	I_{geo}	I_{geo} class[b]
C1	12.2	4	2.3	3	C7	15.3	4	2.5	3
C2	32.1	5	3.7	4	C8	16.7	4	3.0	3
C3	13.3	4	2.6	3	C9	7.1	3	1.3	2
C4	1.8	1	-0.6	0	C10	28.5	5	3.4	4
C5	10.9	4	2.3	3	C11	5.6	3	1.1	2
C6	23.2	4	3.1	4	C12	8.5	3	1.7	2

a. 0: EF <1 (no enrichment), 1: EF <3 (minor), 2: EF = 3–5 (moderate), 3: EF = 5–10 (moderately severe), 4: EF = 10–25 (severe), 5: EF = 25–50 (very severe), and 6: EF >50 (extremely severe) [19].

b. 0: I_{geo} <0 (none), 1: I_{geo} = 0–1 (none to medium), 2: I_{geo} = 1–2 (moderate), 3: I_{geo} = 2–3 (moderately to strong), 4: I_{geo} = 3–4 (strongly polluted), 5: I_{geo} = 4–5 (strong to very strong), and 6: I_{geo} >5 (very strong) [9]

Additionally, the average EF value of 15 obtained in surface sediment is lower than the average EF value of 23.5 reported earlier [17] indicating that the upstream pollution has been reduced so that the accumulation of pollutants in sediments is not as serious as during earlier years. This observation may show the effectiveness of intercepting the Canon River flow and dredging the river mouth.

3.3. Assessment of potential ecological risk

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Cd in surface sediments. PERI that was proposed by Hakanson (1980) [10] can be used to evaluate the potential risk of one metal or combination of multiple metals. The calculated PERI values can be categorized into 5 classes of potential ecological risks: low risk (PERI < 40), moderate risk (40 ≤ PERI < 80), higher risk (80 ≤ PERI < 160), high risk (160 ≤ PERI < 320), and serious risk (PERI ≥ 320). Table 3 and Fig. 2(b) lists the PI value, PERI value, and risk classification for the Cd contained in the surface sediment samples collected near Canon River mouth. Except Station C4 that is classified as moderate risk, all other stations are classified either as serious or high risk with respect to Cd pollution. The above evaluation results indicate that the Cd contained in surface sediment at Canon River mouth has serious potential ecological risks. Therefore, effective management and control of upstream pollution should be immediately implemented in order to improve the river mouth sediment quality and lower the associated ecological risk.

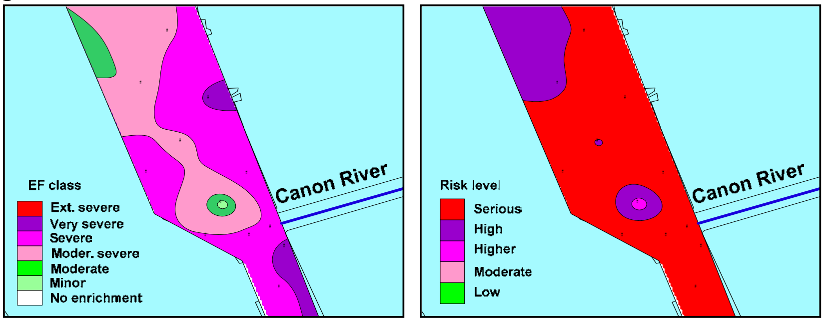

Fig. 4. Enrichment class (a) and potential ecological risk level (b) in surface sediments of Canon River mouth region.

Table 3 Pollution index and potential ecological risk index of Cd in sediments of Canon River mouth

Station	PI	PERI[a]	Risk level	Station	PI	PERI[a]	Risk level
C1	18	544	serious	C7	21	619	serious
C2	48	1444	serious	C8	29	881	serious
C3	23	686	serious	C9	9	281	high
C4	3	75	moderate	C10	39	1163	serious
C5	19	563	serious	C11	8	244	high
C6	33	975	serious	C12	12	356	serious

[a] PERI < 40 indicates low risk, 40 ≤ PERI < 80 is moderate risk, 80 ≤ PERI < 160 is higher risk, 160 ≤ PERI < 320 is high risk, and PERI ≥ 320 is serious risk [10].

4. Conclusions

The surface sediment samples collected at all sampling stations at Canon River mouth contain 0.20–3.85 mg/kg of Cd with an average of 1.74±1.08 mg/kg. The distribution of Cd in surface sediment reveals that the Cd originates from the river upstream discharges of industrial and domestic wastewaters; it is transported along the river and finally deposited and accumulated near the river mouth. Results of EF and I_{geo} analyses indicate that the Canon River mouth sediments were severe contaminated with Cd.

Compared to the EF value of 23.5 reported earlier [17], the degree of Cd enrichment at Canon River mouth has been obviously reduced. This may be associated with river renovation and river mouth dredging. Results of potential ecological risk evaluation show that the classification of potential ecological risk for the sediment Cd at Canon River mouth is between “high risk” to “serious risk”. The results can provide regulatory valuable information to be referenced for developing future strategies to renovate and manage river mouth and harbor.

References

[1] Fukue M, Mulligan CN, Sato Y, Fujikawa T. Effect of organic suspended soilds and their sedimentation on the surrounding sea area. Environmental Pollution 2007; 149:70–8.

[2] Pertsemli E, and Voutsa D. Distribution of heavy metals in Lake Doirani and Kerkini, Northern Greece. Journal of Hazardous Materials 2007; 148:529–37.

[3] Ciliberti A, Berny P, Delignette-Muller ML, and de Buffrénil V. The Nile monitor (Varanus niloticus; Squamata: Varanidae) as a sentinel species for lead and cadmium contamination in sub-Saharan wetlands. Science of the Total Environment 2011; 409:4735–45.

[4] Sparling DW, Linder G, Bishop CA, Krest SK. Ecotoxicology of amphibians and reptiles. 2nd ed. Pensacola: Society of Environmental Toxicology and Chemistry (SETAC); 2010.

[5] Järup L, and Åkesson A. Current status of cadmium as an environmental health problem. Toxicology and Applied Pharmacology 2009; 238:201–8.

[6] Selvaraj K, Ram Mohan V, Szefer P. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. Marine Pollution Bulletin 2004; 49:174–85.

[7] Chen CW, Chen CF, Dong CD, and Tu YT. Composition and Source Apportionment of PAHs in Sediments at River Mouths and Channel in Kaohsiung Harbor, Taiwan. Journal of Environmental Monitoring 2012; in press.

[8] Taylor SR. Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta 1964; 28:1273–85.

[9] Müller G. Schwermetalle in den sediments des Rheins-Veränderungen seit 1971, Umschan 1979; 79:778–783.

[10] Hakanson L. An ecological risk index for aquatic pollution control, a sediment-ecological approach. Water Research 1980; 14:975-1001.

[11] Zhao Q, Xu Q, Yang K. Application of potential ecological risk index in soil pollution of typical polluting industries. Journal of Eastchina Normal University (Natural Science) 2005, 1:110-5.

[12] Yang PM. Distribution and accumulation of heavy metals in sediments of Kaohsiung Harbor. MS thesis, National Kaohsiung Marine University, Taiwan, 2009. p.89.

[13] Birkett JW, Noreng JMK, Lester JN. Spatial distribution of mercury in the sediments and riparian environment of the River Yare, Norfolk, UK. Environmental Pollution 2002; 116:65–74.

[14] Morillo J, Usero J, Gracia I. Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 2004; 55:431–42.

[15] Adamo P, Arienzo M, Imperato M, Naimo D, Nardi G, Stanzione D. Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. Chemosphere 2005; 61:800–9.

[16] Valdés J, Vargas G, Sifeddine A, Ortlieb L, Guinez M. Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23 °S), Northern Chile: geochemical and statistical approach. Marine Pollution Bulletin 2005; 50:1558–1568.

[17] Chen CW, Kao CM, Chen CF, Dong CD. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 2007; 66:1431–40.

[18] Huang KM, and Lin S. Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. Chemosphere 2003; 53:1113–21.

[19] Birth G. A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe, C.D., Furness, R.A. (Eds), Coastal GIS 2003. Wollongong University Papers in Center for Maritime Policy, 14, Australia.